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Calculation of Activation Energy in Discontinuous Thin Metal Films

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Studies of very thin metal films (<100 Å) have shown that they have a distinct island structure. The Neugebauer and Webb theory of conduction[1] in these films assumes that electrons pass from island to island, under the effect of an applied electric field, by tunneling through the inter-island potential barriers. The transfer of electronic charge e between initially neutral islands represents an increase in the system energy and gives rise to an activation energy ϕ. The density of electrons, N_e, with sufficient energy to surmount this electrostatic barrier is given by

$$N_e = N_i \exp -\phi/kT, \tag{1}$$

for $N_e \ll N_i$, i.e., $\phi \gg kT$, where N_i is the island density, k is Boltzmann's constant and T is the absolute temperature. The activation energy ϕ is shown in Fig. 1 as a function of inter-island gap width d, with E_s, the field in the gap, as a parameter.

Analytically, ϕ is given for hemispherical islands of radius r by

$$\phi = (e^2/4\pi\epsilon)[r^{-1} - (r+d)^{-1}] - deE_s, \tag{2}$$

for $E_s < E_{s\,\min}$, and by

$$\phi = (e^2/4\pi\epsilon r) - 2(e^3E_s/4\pi\epsilon)^{1/2} + reE_s, \tag{3}$$

for $E_{s\,\min} < E_s < E_{s\,\max}$, where $E_{s\,\min} = (e/4\pi\epsilon)/(r+d)^2$ and

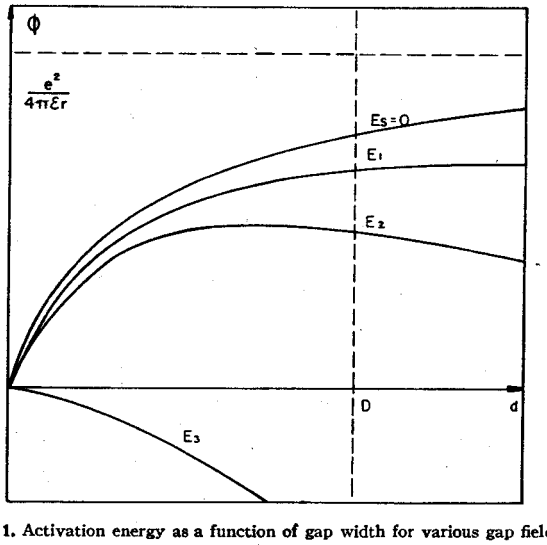

FIG. 1. Activation energy as a function of gap width for various gap fields.

$E_{s\,\max} = (e/4\pi\epsilon)/r^2$. When $E_s > E_{s\,\max}$, ϕ vanishes. For $d = D$ in Fig. 1, ϕ is given by Eq. (2) for $E_s = 0$, E_1 and by Eq. (3) for $E_s = E_2$. The activation energy is zero for $E_s = E_3$.

The conductivity σ is expressed as

$$\sigma = A \exp -\phi/kT, \tag{4}$$

where A is a function of film geometry and the tunneling probability through the inter-island potential barrier.

It is proposed, prior to modification of the basic theory, to establish two geometric parameters in order to characterize a given film with an island structure. The model is idealized to the form of a regular array of hemispherical metal islands of radius r and distance d apart. The two parameters are defined as

$$R = 2r + d \text{ and } p = d/R.$$

Film growth can be separated into three distinct processes.[2] First there is the formation of stable island nuclei[3] of a size characteristic of the deposition conditions and material. When the density of stable nuclei is sufficiently high, no more can be formed and there remains only the growth and coalescence of established islands. The processes can be redefined in terms of R and p. Initial nucleation corresponds to a rapid decrease of R while p changes only slightly. Island growth (the next stage) and coalescence (the final stage) are equivalent respectively to a decrease in p (while R remains constant) and an increase in R (with p nearly constant). It can be seen that the nucleation stage gives way to the process of island growth when no more new sites are formed, i.e., when a critical value of R is reached. This critical value is a function of the critical nucleation size, and therefore of material and deposition conditions, and is the only parameter in the expression for ϕ which can be regarded as a material characteristic.

The gap field E_s is clearly not equal to the applied field E_a since the voltage drop across the islands can be reasonably assumed to be negligible in comparison with that across the gaps. On this assumption, E_s is related to E_a by

$$E_s = E_a/p.$$

Equations (2) and (3) are now restated in terms of E_a as follows:

$$\phi = (e^2/4\pi\epsilon R)\cdot[4p/(1-p^2)] - \mathrm{Re}E_a, \tag{2'}$$

for $E_a < E_{a\,\min}$, and

$$\phi = (e^2/4\pi\epsilon R)\cdot[2/(1-p)] - 2(e^3E_a/4\pi\epsilon p)^{1/2} + \mathrm{Re}E_a(1-p)/2p, \tag{3'}$$

for $E_{a\,\min} < E_a < E_{a\,\max}$, where $E_{a\,\min} = (e/4\pi\epsilon R^2)\cdot 4p/(1+p)^2$

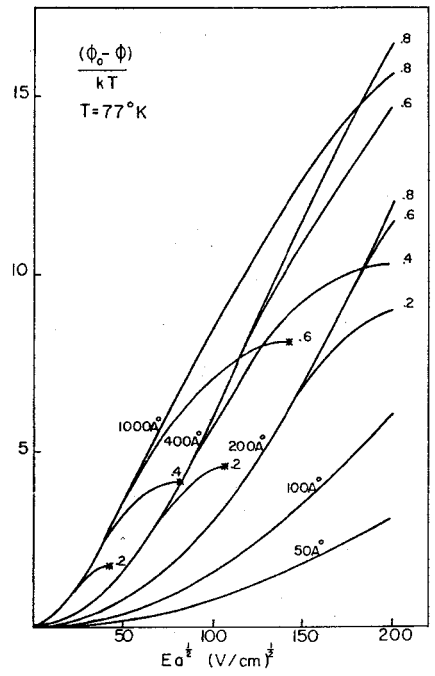

FIG. 2. Log (conductivity/no-field conductivity) as a function of $E_a^{1/2}$ for various film geometries. Note * denotes $\phi=0$.

and $E_{a\,max}=(e/4\pi\epsilon R^2)\cdot 4p/(1-p)^2$. As before, ϕ vanishes when $E_a > E_{a\,max}$.

The reader is now referred to previously published experimental curves for the variation of log σ/σ_0 with applied field[1,4] where σ_0 is the no-field conductivity. Equivalent theoretical curves are presented in Fig. 2.

Both N & W and W & B observed larger values of $\log\sigma/\sigma_0$ with increasing thickness. The immediate implication is that the growth mechanism for the thickness used is one of island coalescence rather than island growth. On the other hand, high-field saturation (W & B) and presaturation linearity (N & W) occur at lower fields for the thicker films implying an island-growth process. There is certainly a mixture of the two processes occurring, but clearly some form of correlation of the results might be made with directly observed film geometry (R and p). Once such correlation has been made, an effective value of ϵ can be estimated. Note that N & W's results show no high-field saturation. It is doubtful whether at the low applied fields (<400 V/cm) they ever exceeded $E_{a\,min}$. Assuming $\epsilon=\epsilon_0$(air), R is estimated (necessarily roughly) at about 400 Å for gold (W & B) and 2000 Å for Ni (N & W). The value for gold is in accordance with direct electron microscope observation of 50–100 Å thick films.

Some conclusions which can be drawn from the theory are worthy of passing mention. The effect of $\epsilon>\epsilon_0$(air) is to reduce $E_{a\,min}$, $E_{a\,max}$, and the increase in conductivity with E_a. As ϕ decreases and approaches kT, the Maxwell–Boltzmann distribution for charge-carrier density is no longer a good approximation and deviations from the simple theory are to be expected.

The verification or rejection of the theory is important for the possible application to Cermet films with an island type of structure, e.g., metal islands in an oxide dielectric. For some of these films it may be necessary to include finite island and dielectric resistivities and the insulating medium dielectric constant will not in general be ϵ_0. Also note that in the above theory, the charge-carrier density only has been dealt with. The mobility or tunneling term A [Eq. (4)] must also be considered if the theory is to be applied to materials research. For this purpose it is proposed to separate the charge-carrier density and mobility terms by means of correlated conductivity and Hall-effect measurements on the samples, using both applied field and temperature as controlled parameters. The results will be interpreted in terms of the geometric parameters R and p giving independent information on the variation of ϕ, N_e, and mobility as function of E_a, R, and p. The electron microscope will be used to find R and p directly for the films. Information on film-growth processes will provide a means of evaluating the validity of the three-stage model of growth. Note that of all the current theories,[5,6] only the N & W model has been considered above, despite its apparent limited applicability.[7] This is because the N & W theory is the most extensively developed and lends itself to the most detailed numerical comparison of theory and experiment.

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